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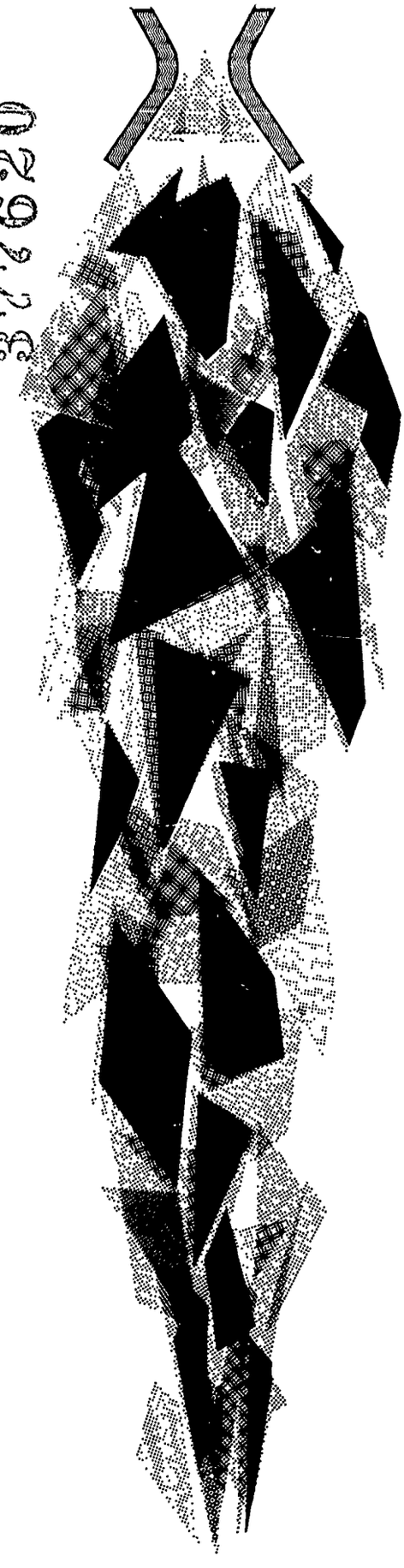

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EVALUATION OF PFG ADDUCTS (u)

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REPORT NO. S-119

EVALUATION OF PFG ADDUCTS (u)

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ABSTRACT

The evaluation of three perfluoroquanidine derivatives prepared by Esso Research Company was carried out using an NF binder system. P-FABDE, FA-TNENE, and FA-PETRIN were added to an NFPA-acrylic acid copolymer/TVOPA binder in varying amounts. A propellant containing 13% P-FABDE proceeded from burning to explosion at pressures of 400 psi and above. High speed motion pictures of burning propellants containing P-FABDE and FA-TNENE showed subsurface combustion of particles, build-up of incandescent streamers on the surface and rate increase through a wormholing or filled void process. Gas voids were produced during the curing reaction of propellants containing over 3% FA-TNENE. Processing difficulties were encountered using FA-PETRIN as plasticizer in place of TVOPA.

Some increase in burning rate was obtained with P-FABDE and FA-TNENE but other considerations, i.e., sensitivity, stability, processing and handling, indicate other methods and materials may be more satisfactory.

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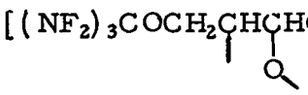
EVALUATION OF PFG ADDUCTS

I. INTRODUCTION

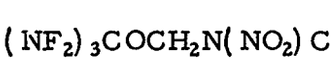
The perfluoroguanidine derivatives listed below were received from Esso Research and Engineering Company for evaluation. The materials are three of the more stable PFG products produced by Esso under Army Missile Command sponsorship.[1] Twenty-five gram samples of each were obtained.

1) Fluorinated PFG adduct of butenediol epoxide polymer,



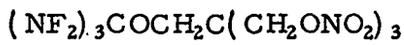
P-FABDE

2) Fluorinated PFG adduct of trinitroethylnitramino-ethanol,



FA-TNENE

3) Fluorinated PFG adduct of pentaerythritol tri-nitrate,



FA-PETRIN

Both P-FABDE and FA-TNENE are relatively thermally-stable solids that are quite impact and friction sensitive. FA-PETRIN is a liquid with an impact sensitivity similar to the other two compounds: 5-10 Kg-cm, 50% fire level on a Picatinny machine.

The compounds were to be investigated in an NF_2 binder propellant made with NFPA-acrylic acid copolymer and TVOPA plasticizer.[2] Strand burning rates, motion pictures of propellant

[1] Esso Research and Engineering Company, "Research on Advanced Solid Propellants," Quarterly Progress Report No. 65-1 (March, 1965), No. 65-2 (June, 1965) and No. 65-3 (September, 1965).

[2] Rohm and Haas Company, Special Report on Preparation and Characterization of NF Prepolymer Propellants, Report No. S-88, October 7, 1965.

burning, impact sensitivity and DTA were to be obtained on compositions where possible. A similar evaluation was made on INFO-635P, a perfluoroguanidine adduct, prepared by the Minnesota Mining and Manufacturing Company.[1,2]

II. RESULTS

P-FABDE

P-FABDE is a relatively thermally-stable solid melting at about 200°C. It is an extremely sensitive material especially to friction and spark, with spark sensitivity ranging from 0.006 joules to 0.05 joules depending upon the physical form of the polymer. Its use in propellant systems would give higher theoretical impulse than could be obtained by available vicinal NF_2 compounds. The P-FABDE would be substituted directly for ammonium perchlorate as a high energy NF oxidizer.

From previous studies at Esso the compatibility of P-FABDE with TVOPA and other vicinal NF compounds was considered adequate for propellant formulation. The concentration of P-FABDE in the propellant formulation was set at approximately 15% initially from both a processability and safety standpoint. Results from the initial composition would determine further work. P-FABDE was investigated in two propellant compositions, with one propellant containing 13% P-FABDE, the other containing 5% P-FABDE. The propellants were made with NFPA-acrylic acid copolymer and TVOPA plasticizer binder system. P-FABDE was never isolated as neat material during the investigation.

The P-FABDE was added to the propellant mixture by stripping the Freon® -113 solution in the presence of the NFPA-acrylic acid-TVOPA mixture. The Freon-113 caused precipitation of

[1] Chemical Propulsion Information Agency Publication No. 97, INFO-635P Meeting, May 19, 1965.
[2] Rohm and Haas Company, Quarterly Progress Report on A.R.P.A. Projects, P-64-19, October, 1964.
® Trademark of E.I. DuPont de Nemours and Co., Wilmington, Delaware.

the NFPA-acrylic acid copolymer but the polymer redissolved when the Freon was removed. The P-FABDE also precipitated as the Freon was removed but it did not entirely redissolve.

Fifty grams of the following composition was prepared:

RH-SE-197-01

Ammonium perchlorate, 110-115μ	29.5% Wt.
Aluminum, Alcoa 140	9.5
NFPA-acrylic acid copolymer	16.0
TVOPA	32.0
P-FABDE	13.0
Unox 221®	2.0 (added)

The composition mixed and cast satisfactorily, but contained small lumps throughout, probably undissolved P-FABDE. It was cured at 60°C. for sixteen hours. The cured propellant had satisfactory qualitative physical properties, but contained specks of polymer throughout. The following impact sensitivity was obtained on the Picatinny Arsenal machine: 50% fire level 4-5 in., 1 kilo weight; RDX = 10 in.

SE-197-01 was burned in the Crawford bomb at atmospheric pressure and at pressures up to 500 psi. Strands at the higher pressures deflagrated very rapidly and burning rates were obtained only at atmospheric pressure and 100 psi. At 200 psi normal burning started and then proceeded to explosion. A sample was submitted for window-bomb studies and normal burning was observed in the window bomb up to 400 psi. At pressures above 400 psi, however, the change from burning to explosion occurred in one frame of motion picture film taken at 3000 frames per second. Some discrepancy in burning rates was noted and will be discussed later.

® A diepoxide curing agent supplied by Union Carbide Chemical Company, New York, N.Y.

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A second composition was prepared containing 5% P-FABDE:

RH-SE-205-1

NH_4ClO_4, 110-115μ	37% Wt.
Aluminum	10
NFPA-acrylic acid copolymer	16
TVOPA	32
P-FABDE	5
Unox 221	2 (added)

The P-FABDE was again stripped from the Freon-113 solution in the presence of the NFPA polymer-TVOPA mixture. The P-FABDE appeared to be partly dissolved in the mixture with no large particles of polymer visible. The compositions mixed, cast and cured satisfactorily. Impact sensitivity obtained on the Picatinny Arsenal machine: 50% fire 7 in., 1 kilo weight.

Strand burning rates in a closed bomb gave the following:

RH-SE-205

500 psi	1.40 in./sec.
1000 psi	2.08 in./sec.
2000 psi	3.32 in./sec.

n = 0.65

Window-bomb motion pictures gave the following rates for SE-205:

500 psi	1.04 in./sec.
1000 psi	1.56 in./sec.
2000 psi	2.42 in./sec.

The rates from the motion pictures were calculated for distances where the burning surface was horizontal and smooth. When cavitation or gross irregularities occurred the measurement was stopped and the rate calculated; however, closed bomb strand rates were measured over a set distance and degree of cavitation or wormholing effect could not be determined.

Window-bomb motion picture burning rates obtained from a composition similar to SE-205 without P-FABDE gave essentially the same burning rates as that with 5% P-FABDE, meaning that the rate augmentation observed from strand burning studies took place through a filled-void or wormholing mechanism; i.e., no catalytic effect was present.

The composition containing 13% P-FABDE showed burning coloration similar to the blue color produced with INFO 635P. Incandescent particles also built up on the surface into streamers before falling away. The 5% P-FABDE composition flame had some blue color but no build-up of worm-like particles, possibly because of the better dispersion of the P-FABDE.

FA-TNENE

FA-TNENE is a stable solid melting at 101-103°C. which is not quite as sensitive to impact, friction or spark as P-FABDE. FA-TNENE was incorporated in propellant compositions by two methods. One method was to add the material dissolved in methylene chloride to the liquid binder materials and strip off the solvent before adding ammonium perchlorate and aluminum. The other method was to add dry, neat FA-TNENE to the binder materials and then add perchlorate and aluminum.

The first composition tried was made by the solvent addition method and contained 15% FA-TNENE:

RH-SE-211

NH_4ClO_4	30%
Aluminum	10
NFPA/AA	15
TVOPA	30
FA-TNENE	15
Unox 221	2 (added)

The mixture was cured at 60°C. for 16 hours. The cured propellant contained many gas voids throughout the entire slab. No burning rates could be obtained. The next composition was also

made by the solvent addition method but with only 5% FA-TNENE instead of 15%. The cured propellant also had many small voids similar to the 15% composition, only fewer in number.

The addition of dry, neat FA-TNENE at the 2.5% level to a propellant composition was attempted and resulted in a void-free slab with adequate physical properties.

RH-SE-227

NH_4ClO_4	45%
Aluminum	10
NFPA/AA	14
TVOPA	29
FA-TNENE	2.5 (added)
Unox 221	2

The FA-TNENE appeared to be well dispersed with no discrete particles visible. The propellant was burned in the micro window bomb, giving the following photographically determined burning rates.

Pressure, psig	Rate, in./sec.
500	0.80
1000	1.3 uneven surface
1500	1.7

These give a burning rate pressure exponent of 0.7.

One unusual feature noted in the movies was incandescent particles that built up on the burning surface into streamers before falling away. The effect was similar to that obtained with 13% P-FABDE but much larger streamers were produced. Another effect noted from the films was that, at the higher pressures, black puffs of material were ejected from the surface. These undoubtedly resulted from sub-surface decomposition of the FA-TNENE or surrounding material. As with the other PFG adducts this could present a problem, especially at higher pressures, if the adduct was present in high concentrations or was not well dispersed. Esso Research Company, however, has been able to incorporate up to 60% FA-TNENE and obtain smooth burning.

One further attempt was made to incorporate 10% FA-TNENE in a propellant composition:

RH-SE-231

NH_4ClO_4	35%
Aluminum	10
NFPA/AA	15
TVOPA	30
FA-TNENE	10
Unox 221	2 (added)

The FA-TNENE was isolated from the chloroform solvent, dried under a vacuum of 1 mm or less for 24 hours, and added to the prepolymer-TVOPA mixture in which it appeared to be soluble. The complete propellant mixture was cured at 60°C. for 40 hours. The cured propellant slab had adequate physical properties but contained many small voids similar to previous FA-TNENE propellants. The results obtained with FA-TNENE indicate a reaction between it and some propellant ingredient or impurities. The one successful composition prepared contained the least amount of FA-TNENE and the decomposition gases were probably produced in amounts that were absorbed by the solid mass.

Impact sensitivity of FA-TNENE propellants was similar to that of propellants containing other NF_2 compounds: 8-10 in., 50% fire level, 1 kg. weight.

FA-PETRIN

FA-PETRIN was planned for use as plasticizer for NFPA/acrylic-acid copolymer binder system to provide a direct comparison with TVOPA. Preliminary results indicated that RH-SE-230 should be a suitable formulation and a 100-gram batch was made.

RH-SE-230

NH_4ClO_4	46%
Aluminum	15
NFPA/AA	13
FA-PETRIN	26
Unox 221	1.8 (added)

It was planned to cast the propellant into 0.75C.5-1.5 micro-motors, but the propellant slurry was quite viscous, cast with difficulty, and gelled before the motors were completely full. No usable motors were obtained. Examination of the cured propellant revealed the presence of voids so that no burning rate data were obtained. Due to the high viscosity of the mix, the voids may have been caused by air entrapped during casting. Some material was removed from a motor and impact sensitivity was obtained.

	SE-230 (FA-PETRIN)	SE-103 (TVOPA)
50% Fire Level		
1 Kg Wt.	8.0 in.	8.0 in.

The propellant batch used the entire supply of FA-PETRIN so no further comparison with TVOPA was obtained.

III. SUMMARY

The use of PFG adducts in propellant formulations was investigated in an NF binder system at several concentrations, and the results are summarized briefly.

P-FABDE

Stable burning could not be obtained in a propellant containing 13% P-FABDE at pressures above 400 psi. A propellant with 5% P-FABDE produced an increase in burning rate through a filled void-wormholing technique.

Motion pictures of the burning propellant showed features similar to those obtained with INFO 635P, i.e., blue color, fast burning or exploding particles depending on size and pressure. A new feature was the build-up of incandescent streamers on the burning surface.

FA-TNENE

Difficulties were encountered in the curing reaction of propellants containing FA-TNENE. Concentrations of 5% and above resulted in gas void formation during curing. A propellant containing approximately 2% FA-TNENE was prepared and motion pictures of the

burning propellant showed features similar to INFO 635 and P-FABDE. The build-up of incandescent particles was more pronounced than with P-FABDE. The use of FA-TNENE in the acid-epoxide cured binder system used for these propellants produced an undesirable side reaction in concentrations above 3%.

FA-PETRIN

From limited studies FA-PETRIN was found to be considerably more viscous than TVOPA and to cause propellant processing difficulties. Impact sensitivity of a FA-PETRIN propellant was the same as that of the corresponding TVOPA compositions.

IV. CONCLUSIONS

PFG derivatives may be used in difluoramino binder system propellants with the proper choice of concentration and particle size. The use of P-FABDE in concentrations above 10% is probably not practical due to the tendency to proceed from burning to explosion. Concentrations of FA-TENE above 3% resulted in a gas producing reaction during curing which voided any ballistic evaluation. Processing difficulties due to high viscosity were experienced when FA-PETRIN was used as plasticizer in a direct substitution for TVOPA.

Some burning rate increase can be obtained with the PFG compounds at certain concentrations and particle sizes; however, there is a tendency to go from burning to explosion at high concentrations and large particle size. The extreme sensitivity of the PFG adducts to impact, friction and spark make propellant processing difficult and the increase in burning rate produced may well be obtained by other less sensitive materials and methods.

V. GLOSSARY

FA-PETRIN - Fluorinated PFG adduct of pentaerythritol trinitrate.

FA-TNENE - Fluorinated PFG adduct of trinitroethylnitraminoethanol.

INFO-635P - tris(difluoramino) methoxyethyl ammonium perchlorate.

NFPA/AA - 2,3-bis(difluoramino) propyl acrylate/acrylic acid copolymer.

P-FABDE - Fluorinated perfluoroguanidine adduct of butenediol epoxide polymer.

TVOPA - 1,2,3-tris-1,2-bis(difluoramino) ethoxy propane.

UNOX 221 - Diepoxide supplied by Union Carbide Chemical Company.